



# Ruthenium(0) nanoclusters stabilized by zeolite framework as superb catalyst for the hydrogenation of neat benzene under mild conditions: Additional studies including cation site occupancy, catalytic activity, lifetime, reusability and poisoning

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## ABSTRACT

The hydrogenation of arenes is an ubiquitous chemical transformation used in both the petrochemical and specialty industry and important for the generation of clean diesel fuels. In a recent communication (M. Zahmakiran, S. Özkar, *Langmuir* 24 (2008) 7065) we have reported the preliminary results for the unprecedented catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene ( $TOF \approx 1040$  mol benzene/mol Ru-h) under mild conditions ( $22^\circ C$ ,  $40 \pm 1$  psig  $H_2$ ). Here we report the work in full details, including (i) far-infrared spectroscopic investigation of ruthenium(III)-exchanged-zeolite and zeolite framework containing ruthenium(0) nanoclusters, which showed that ruthenium(0) nanoclusters formed inside the cavities of zeolite by retaining its framework intact, (ii) the collection of wealthy kinetic data to demonstrate the effect of ruthenium loading, temperature, and catalyst concentration on the catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene, (iii) probing the isolability, bottleability and reusability of zeolite framework stabilized ruthenium(0) nanoclusters; (iv) poisoning experiments performed by using tricyclohexylphosphine ( $P(C_6H_{11})_3$ ) and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ( $P(OCH_2)_3CCH_2CH_3$ ) in order to answer the most classical question whether the ruthenium(0) nanoclusters exist on the surface or inside the cavities of the host material; (v) a summary section detailing the main findings for the “green chemistry”.

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## 1. Introduction

The complete hydrogenation of arenes is one of the most important and challenging transformations in the synthesis of fine chemicals and intermediates [1] and traditionally has been carried out under high temperature and/or high pressure conditions (i.e., around and above  $100^\circ C$  and 50 atm  $H_2$ ) [2]. A literature review (SciFinder literature search for the Keywords: “benzene hydrogenation” resulted in  $>1900$  hits) reveals that a range of homogeneous and heterogeneous catalysts have been used to hydrogenate benzene; which is a common test reaction for the arene hydrogenation catalysts. Among these the best catalytic systems yielding complete hydrogenation of benzene without any side products under mild conditions ( $\leq 25^\circ C$ ; and  $\leq 3$  atm  $H_2$ ) are hydroxylalkylammonium bromide-stabilized rhodium(0) nanoclusters [3–5]; hydroxylalkylammonium chloride-stabilized

iridium(0) nanoclusters [6]; cyclodextrins-stabilized rhodium(0) nanoclusters [7]; rhodium(0) nanoclusters immobilized on silica [8]; tethered Rh(COD) units anchored to polymers [9]; rhodium(0) nanoclusters entrapped in boehmite nanofibers [10]; ruthenium(0) nanoclusters immobilized into SBA-15 [11];  $[(Cp^*)_2Zr(CH_3)_2]^+$  activated via super acidic sulfated alumina or sulfated zirconia [12]. Except the last one; the most important general feature of those catalytic systems is the use of transition metal nanoclusters’ catalysts. Transition metal nanoclusters have attracted much attention in organic synthesis due to their distinct catalytic activities in various transformations [13]. However; in their catalytic application one of the most important problems is the aggregation of nanoclusters into clumps and ultimately to the bulk metal; despite using the best stabilizers [14,15]; which leads to a decrease in catalytic activity and lifetime. The use of nanoclusters catalysts in systems with confined void spaces such as inside mesoporous and microporous solids appears to be an efficient way of preventing aggregation [16,17]. Moreover; metal nanoclusters catalyst encapsulated within the cavities of zeolite or between the zeolite-supported layers (i.e., zeolite films; powders or membranes supported on the

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surface of solid materials) [18] may provide kinetic control for the catalytic reactions. Expectedly; a recent communication has reported that the zeolite framework stabilized ruthenium(0) nanoclusters provide a record catalytic activity in the hydrogenation of neat benzene under mild conditions (at 22 °C; 40 ± 1 psig H<sub>2</sub>) [19]. Zeolite framework stabilized ruthenium(0) nanoclusters were easily prepared at room temperature by borohydride reduction of Ru<sup>3+</sup>-exchanged-zeolite-Y and characterized by using a combination of advanced analytical techniques including XRD; HR-TEM; XRD; HRTEM; TEM-EDX; SEM; XPS; ICP-OES; and N<sub>2</sub> adsorption; which were previously reported [20]. Herein we report; in particular; the far-IR investigation of the zeolite framework containing ruthenium(III) ions or ruthenium(0) nanoclusters. The comparison of frequencies and intensities of cation translatory modes in the far-IR spectra of zeolite-Y; Ru(III)-exchanged-zeolite-Y; and zeolite framework stabilized ruthenium(0) nanoclusters show that; after the reduction of the Ru<sup>3+</sup> ions in the cavities of zeolite-Y with sodium borohydride in aqueous solution; the Na<sup>+</sup> ions reoccupy the cation sites left by the Ru<sup>3+</sup> ions upon reduction. More importantly; far-IR analyses provide a compelling evidence for the integrity of the zeolite framework after the procedure used for the preparation of nanoclusters within the cavities of zeolite. In this paper; we also report in full detail the results of kinetic study on the hydrogenation of neat benzene catalyzed by zeolite framework stabilized ruthenium(0) nanoclusters depending on ruthenium loading; temperature; and catalyst concentration. Further experiments show that the zeolite framework stabilized ruthenium(0) nanoclusters are isolable, bottleable, redispersible and yet catalytically active. They retain 81% of their initial activity at the fifth run with the complete hydrogenation of neat benzene under mild conditions (at 22 °C; 40 ± 1 psig H<sub>2</sub>). Moreover; they fulfil most of the requirements in one of the most important "Green Chemistry" proposals [21] which imposes neat/solventless systems whenever possible. There are only 5 neat benzene hydrogenation studies in the literature that have been employed ≤25 °C with complete conversion into cyclohexane [9–12]. The work reported here also includes poisoning experiments performed by using the large tricyclohexylphosphine (P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>) or the compact 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>) to determine the distribution of ruthenium(0) nanoclusters between the cavities and the external surface of zeolite.

## 2. Experimental

### 2.1. Materials

Ruthenium(III) chloride trihydrate (RuCl<sub>3</sub>·3H<sub>2</sub>O), sodium borohydride (98%), benzene (99%), toluene (99%), *d*-Chloroform (CDCl<sub>3</sub>) and cyclohexane (99%) were purchased from Aldrich. Cyclohexene (99%), mesitylene (98%), and *o*-xylene (98%) were purchased from Fluka. Sodium zeolite-Y (Na<sub>56</sub>Y, Si/Al=2.5) was purchased from Zeolyst and slurried with 0.1 M NaCl to remove sodium defect sites, washed until free of chloride and calcined in dry oxygen at 500 °C for 12 h before to use. Tricyclohexylphosphine (P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>) and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>) were purchased from Ventron and Fluka, respectively. All catalyst reaction solutions were prepared in oxygen free atmosphere (Labconco, drybox). Cyclohexane, cyclohexene, benzene, toluene, mesitylene and *o*-xylene were distilled over sodium under argon and stored in the drybox. Ruthenium(III) chloride was recrystallized from water and the water content of RuCl<sub>3</sub>·*x*H<sub>2</sub>O was determined by TGA and found to be *x*=3. Deionized water was distilled by water purification system (Milli-Q System). All glassware and Teflon coated magnetic stir

bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

### 2.2. Preparation of zeolite framework stabilized ruthenium(0) nanoclusters

Zeolite framework stabilized ruthenium(0) nanoclusters were synthesized by following a two-step procedure; (i) in the first step, ruthenium cations were introduced into the zeolite-Y by ion-exchange [22] of 500 mg zeolite-Y in 100 mL aqueous solution of 20.7 mg RuCl<sub>3</sub>·3H<sub>2</sub>O (for 0.80 wt% loading) for 72 h at room temperature. The sample was then filtered by suction filtration using Whatman-1 filter paper, washed three times with 20 mL of deionized water and the remnant was dried in vacuum. (ii) In the second step, the solid remnant was added into 100 mL NaBH<sub>4</sub> solution (568 mg, 150 mM) at room temperature. Ruthenium(III) ion was reduced and the ruthenium(0) nanoclusters were formed; the reduction was considered to be complete when no more hydrogen evolution was observed. The zeolite framework stabilized ruthenium(0) nanoclusters sample was filtered again by suction filtration using Whatman-1 filter paper, washed three times with 20 mL of deionized water, and dried under N<sub>2</sub> gas purging at room temperature for 24 h, then transferred into the drybox (O<sub>2</sub><5 ppm, H<sub>2</sub>O<1 ppm).

### 2.3. Pretreatment of samples and measurement conditions for far-IR studies

In the preparation of the samples for far-IR analyses; ruthenium(III)-exchanged-zeolite-Y and its reduced form, zeolite framework stabilized ruthenium(0) nanoclusters, were prepared by following the procedure described in the previous section. The concentration of the aqueous solution was adjusted to control the degree of ion-exchange and the ruthenium content in the sample. The ruthenium and sodium contents of the solid samples (vacuum dried) were determined by ICP-OES. The zeolite powder samples were pressed into self-supporting wafers of 15 mm diameter weighing approximately 15 mg by using an applied pressure of 6–8 tons per square inch for up to 60 s. The wafers were clamped into a glass tube whose one-side turbomolecular vacuum (10<sup>-7</sup> Torr) connected and located in furnace. Thus the self-supporting wafers were dehydrated with the following heating schedule, using an NX-(Mitsubishi) series temperature controller: 0.5 h from 25 to 100 °C, 1 h at 100 °C, 4 h from 100 to 550 °C and 4 h at 550 °C. After thermal treatment the samples inside the glass tube were cooled down to room temperature, then sealed and transferred into the glove box (O<sub>2</sub><5 ppm, H<sub>2</sub>O<1 ppm) in which the sample was put into a sample holder equipped with high density polyethylene window. The level of dehydration was checked by complementary Mid-IR spectroscopy. The degree of dehydration was judged by the flatness of the baseline in the IR v(OH) stretching and δ(OH) deformation regions, 3400–3700 and 1600–1650 cm<sup>-1</sup>, respectively, and was found to be complete in all cases. The far-IR spectra were recorded at Nicolet Magna-IR 750 spectrometer under N<sub>2</sub> purging by using global source and DTGS detector. The spectral resolution in all cases was 4 cm<sup>-1</sup> and all of the spectra have been base line corrected.

### 2.4. Hydrogenation apparatus

Hydrogenation reactions were performed using hydrogenation apparatus; a Fischer–Porter pressure bottle modified by Swagelock TFE-sealed quick-connects and connected to a H<sub>2</sub> line and a Omega PX-302 pressure transducer interfaced through an Omega D1131 digital transmitter to a computer using the RS-232 module. The progress of individual hydrogenation reactions was

followed by monitoring the loss of H<sub>2</sub> pressure on Lab View 8.0 program.

## 2.5. Hydrogenation experiments and calculation of reaction rates

A similar procedure as described elsewhere was followed here [19,20]. All reaction mixtures were prepared in a nitrogen-filled oxygen free drybox (O<sub>2</sub> < 5 ppm, H<sub>2</sub>O < 1 ppm). In a drybox the catalyst was weighed into 40 mm × 20 mm borosilicate culture tube containing 5/16 in. × 5/8 in. Teflon coated magnetic stir bar then the substrate was transferred into this tube via gas-tight syringe. The culture tube was then sealed inside of the Fischer–Porter pressure bottle and Fischer–Porter bottle brought outside of the drybox and placed inside a constant temperature circulating water bath. Next the hydrogenation line was evacuated for at least 1 h, to remove any trace of oxygen and water present and then the line was refilled with purified hydrogen. The Fischer–Porter bottle was then attached to the hydrogenation line via its TFE-sealed Swagelock Quick-Connects and the bottle was purged 10 times (15 s per purge). A timer was started and the pressure in the F–P bottle was then set a constant 40 ± 1 psig of H<sub>2</sub>. The reaction was monitored on PC via RS-232 module and using Lab View 8.0 program. Reaction rates were calculated from the rate of hydrogen pressure loss as determined by the slope of the linear portion of the H<sub>2</sub> uptake curve.

## 2.6. Control experiment (1): detection of mass-transfer limitation in the hydrogenation of cyclohexene catalyzed by zeolite framework stabilized ruthenium(0) nanoclusters

To obtain intrinsic kinetic data independent of external diffusion effects eleven experiments in the hydrogenation of 0.5 mL cyclohexene (in 1.5 mL cyclohexane) catalyzed by 100 mg zeolite framework stabilized ruthenium(0) nanoclusters (with a ruthenium loading of 0.68 wt% corresponds to 0.0067 mmol ruthenium) were conducted at 22 ± 0.1 °C and 40 ± 1 psig H<sub>2</sub> using different stirring speeds. It was found that up to 600 rpm MTL regime is effective on the observed rate for the hydrogenation of cyclohexene. Therefore, in all the catalytic tests reported hereafter the stirring speed was adjusted to >720 rpm.

## 2.7. Catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of olefins and arenes

In a series of experiments the catalytic activity of 100 mg zeolite framework stabilized ruthenium(0) nanoclusters (with a ruthenium content of 1.4 wt%) were tested in the hydrogenation of cyclohexene, toluene, benzene, *o*-xylene, and mesitylene in cyclohexane (0.5 mL substrate + 2.5 mL of cyclohexane) at 22 ± 0.1 °C and 40 ± 1 psig H<sub>2</sub>.

## 2.8. Control experiment (2): checking the catalytic activity of zeolite-Y (Na<sub>56</sub>Y) in the hydrogenation of neat benzene

To investigate the effect of the host material zeolite-Y on the catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters, the hydrogenation of 2.0 mL benzene (22.4 mmol) was performed in the presence of 500 mg zeolite-Y (corresponds to maximum amount of zeolite-Y that used as a host material in all the experiments reported here). The same experiment was repeated at different temperatures (15, 20, 25, 30, and 35 °C).

## 2.9. Catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene depending on ruthenium loading (wt%)

The catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters ([Ru] = 10 mM) with a various ruthenium loading in the range of 0.4–8.4 wt% Ru were tested in the hydrogenation of 1.0 mL benzene (11.2 mmol) at 22 ± 0.1 °C.

## 2.10. The catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene depending on ruthenium concentration

In a series of experiments the hydrogenation of 1.0 mL benzene (11.2 mmol) was performed in the presence of 22.3, 44.6, 66.9, 89.2, 111.5 and 133.8 mg zeolite framework stabilized ruthenium(0) nanoclusters (with a ruthenium loading of 0.95 wt% corresponds to 2, 4, 6, 8, 10 and 12 mM Ru in 1.0 mL benzene) at 22 ± 0.1 °C, 40 ± 1 psig of H<sub>2</sub>.

## 2.11. Catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene depending on temperature

To obtain the activation energy (E<sub>a</sub>) the hydrogenation of 0.60 mL benzene (6.72 mmol) was performed in the presence of 64 mg zeolite framework stabilized ruthenium(0) nanoclusters (with a ruthenium loading of 1.1 wt% corresponding to 0.0069 mmol Ru) at 15, 20, 25, 30, 35 °C, 40 ± 1 psig of H<sub>2</sub>.

## 2.12. Catalytic lifetime of zeolite framework stabilized ruthenium(0) nanoclusters catalyst in the hydrogenation of neat benzene

In the nitrogen-filled drybox, 100 mg zeolite framework stabilized ruthenium(0) nanoclusters (with a ruthenium loading 1.4 wt%) was weighed into a new culture tube containing a new stirring bar then 3.0 mL benzene (33.6 mmol benzene corresponding to a maximum turnover number of 2426 mol benzene/mol Ru) was added via 5.0 mL gas-tight syringe into the culture tube. The experiment was performed in the same way as described previously and more H<sub>2</sub> has been added to the FP bottle (not >40 psig for each addition) when the pressure inside lowers down to ~20 psig as monitored via computer interface.

## 2.13. Isolability and reusability of zeolite framework stabilized ruthenium(0) nanoclusters catalyst in the hydrogenation of neat benzene

After the first run of the hydrogenation of 0.8 mL benzene (8.96 mmol), catalyzed by 100 mg zeolite framework stabilized ruthenium(0) nanoclusters (with a ruthenium loading of 0.95 wt% corresponding to 0.0094 mmol Ru) at 22.0 ± 0.1 °C, 40 ± 1 psig of H<sub>2</sub>, the FP bottle was disconnected from the line, taken into the drybox, opened and the content of the culture tube was transferred into the Schlenk tube, resealed and connected to vacuum line. After the evaporation of volatiles, the Schlenk tube was transferred into the glove box. After 1 day the solid residue of zeolite framework stabilized ruthenium(0) nanoclusters was weighed and used again in the hydrogenation of 0.8 mL benzene (8.96 mmol). The same procedure was repeated three times after 1 week, 15 days and 1 month. In addition to hydrogen uptake data, the <sup>1</sup>H NMR spectrum of reaction solutions taken at the end of each run showed that the benzene is completely converted to cyclohexane (1.44 ppm). Results of the NMR experiment clearly showed that there is no detectable unreacted benzene nor partially hydrogenated products. The results

were expressed as a percentage of initial catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene.

#### 2.14. The leaching test of zeolite framework stabilized ruthenium(0) nanoclusters

After the first run of hydrogenation of 0.8 mL benzene (8.96 mmol), catalyzed by 100 mg zeolite framework stabilized ruthenium(0) nanoclusters (with a loading of 0.95 wt% Ru corresponding to 0.0094 mmol Ru) at  $22.0 \pm 0.1^\circ\text{C}$  and  $40 \pm 1$  psig of  $\text{H}_2$ , the FP bottle was disconnected from the line, taken into the drybox, opened and the suspension in the culture tube was filtered. The filtrate was transferred into a new culture tube with 0.5 mL fresh benzene. The culture tube was placed into the FP bottle. The hydrogenation of benzene was performed in the same way as described previously. No hydrogenation of benzene was observed after 12 h. Additionally, no ruthenium metal was detected in the filtrate by ICP (detection limit is 24 ppb for Ru).

#### 2.15. $\text{P}(\text{C}_6\text{H}_{11})_3$ and $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ poisoning of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene

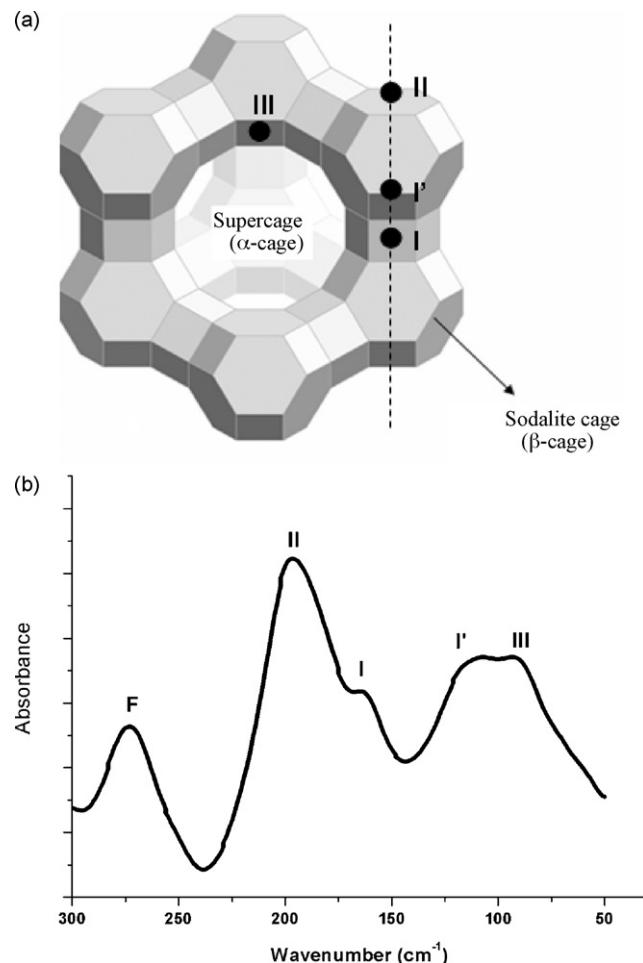
In order to begin the catalyst poisoning experiments a stock solution of  $\text{P}(\text{C}_6\text{H}_{11})_3$  in benzene was prepared by dissolving 1.49 g in 9.5 mL benzene in drybox. Then, 128 mg of catalyst (0.95 wt% Ru loaded) was transferred into a 22 mm  $\times$  175 mm culture tube containing a  $5/16$  in.  $\times$   $5/8$  in. Teflon coated magnetic stir bar. To this was added an aliquot (24–720  $\mu\text{L}$ ) of either  $2.6 \times 10^{-5}$  M or a  $8 \times 10^{-4}$  M  $\text{P}(\text{C}_6\text{H}_{11})_3$  stock solution (in benzene) using a 500  $\mu\text{L}$  gas-tight syringe and the total volume of solution in the culture tube was adjusted to 1.5 mL by adding benzene (1.476–0.78 mL). The culture tube was then placed in the Fischer–Porter bottle, sealed, taken out of the drybox, placed in a constant temperature circulation water bath thermostated at  $22 \pm 0.1^\circ\text{C}$  and attached to the hydrogenation apparatus via the quick-connects and stirred for a 10 min before the pressure was set to  $40 \pm 1$  psig of  $\text{H}_2$ . The same protocol was also followed by using  $1.2 \times 10^{-6}$ – $3 \times 10^{-6}$  mol  $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ .

### 3. Results and discussions

#### 3.1. Preparation of the zeolite framework stabilized ruthenium(0) nanoclusters and far-IR investigation of the changes in cation site occupancy during the preparation

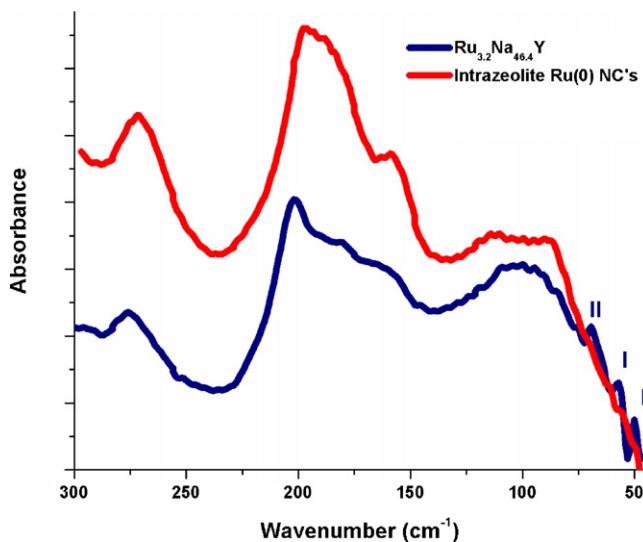
Zeolite framework stabilized ruthenium(0) nanoclusters, hereafter referred to as Ru(0)/NaY, were prepared by ion-exchange [22] of  $\text{Ru}^{3+}$  ions with the extra-framework  $\text{Na}^+$  ions of zeolite-Y, followed by reduction of the  $\text{Ru}^{3+}$  ions in the cavities of zeolite-Y with sodium borohydride in aqueous medium all at room temperature. Following the two-step procedure, zeolite-Y is first added to the aqueous solution of ruthenium(III) chloride in the equivalent amount corresponding to the degree of ion-exchange and the suspension is stirred for three days at room temperature. After filtering, copious washing with water,  $\text{Ru}^{3+}$ -exchanged-zeolite-Y was reduced by sodium borohydride in aqueous solution yielding Ru(0)/NaY without causing alteration in the framework lattice, mesopores' formation, or loss in the crystallinity of the host material as determined by ICP-OES, XRD, XPS, SEM, TEM, HRTEM, TEM/EDX and  $\text{N}_2$  adsorption–desorption analyses [19,20].

The far-infrared spectroscopy is a vital tool to directly probe the cation sites in the zeolite via their characteristic vibrational modes [23]. The combined use of the frequencies and intensities of site specific metal cation absorption bands in the far-IR spectrum allows us to secure metal cation vibrational assignments for sites



**Fig. 1.** (a) Schematic view of the structure of zeolite-Y ( $\text{Na}_{56}\text{Y}$ ), (b) far-IR spectrum ( $325$ – $25\text{ cm}^{-1}$ ) of vacuum thermally dehydrated ( $10^{-7}$  Torr,  $550^\circ\text{C}$ ) zeolite-Y with  $\text{Si}/\text{Al} = 2.5$ . The cation site assignments discussed in the text are shown on the bands. F denotes an oxygen framework vibration.

I–III and I' in zeolite-Y as shown in Fig. 1(a) [24]. Fig. 1(b) shows the far-IR spectrum ( $300$ – $25\text{ cm}^{-1}$ ) of vacuum thermally dehydrated zeolite-Y with band assignments to cation sites [23,24]. This assignment of the extra-framework cation sites in zeolite-Y has also been confirmed by  $^{23}\text{Na}$  NMR spectroscopy [25–28]. It has been shown that there are normal modes of the charge balancing cations which can be considered to be essentially decoupled from the lattice vibrations [23]. Each cation site has a vibrational mode with characteristic frequency in the far-IR region as shown in Fig. 1(b). The frequencies of cation translatory vibrational modes depend on the mass and charge of the cation [23]. Since  $\text{Ru}^{3+}$  is trivalent and also heavier than  $\text{Na}^+$  its modes are expected to be at lower frequencies than those of  $\text{Na}^+$ . The far-IR spectra of  $\text{Ru}^{3+}$ -exchanged-zeolite-Y with a nominal composition of  $\text{Ru}_{3.2}\text{Na}_{46.4}\text{Y}$  and Ru(0)/NaY are given in Fig. 2. On passing from  $\text{Na}_{56}\text{Y}$  to  $\text{Ru}_{3.2}\text{Na}_{46.4}\text{Y}$  the site I, I', and II  $\text{Na}^+$  cation bands in the far-IR spectra lose intensity while three lower frequency bands grow in at  $79$ ,  $67$  and  $57\text{ cm}^{-1}$ , which are readily assigned to the  $\text{Ru}^{3+}$  cation translatory modes. Comparison of the vibrational spectra of the other zeolite-Y samples with different cations [23–25] shows that the frequency order  $\text{II} > \text{I} > \text{I}'$  of cation site absorptions caused by one cation type in different sites is retained. These results reflect the occupancy of cation sites in both  $\alpha$  and  $\beta$  cages by ruthenium(III) ions and the three major sites occupied are probably II, I and I'. The far-IR spectrum of Ru(0)/NaY prepared by the sodium borohydride reduction of  $\text{Ru}^{3+}$ -exchanged-zeolite-Y sample ( $\text{Ru}_{3.2}\text{Na}_{46.4}\text{Y}$ ) shows that the

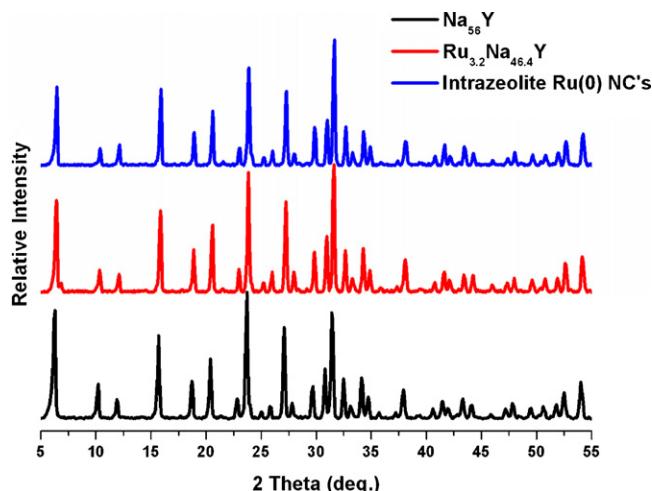


**Fig. 2.** The far-IR spectra of vacuum thermally dehydrated ( $10^{-7}$  Torr,  $550^\circ\text{C}$ ) sample of  $\text{Ru}^{3+}$ -exchanged-zeolite-Y ( $\text{Ru}_{3.2}\text{Na}_{46.4}\text{Y}$ ) (blue, bottom) and  $\text{Ru}(0)/\text{NaY}$  (red, top) prepared by the borohydride reduction of  $\text{Ru}^{3+}$ -exchanged-zeolite-Y ( $\text{Ru}_{3.2}\text{Na}_{46.4}\text{Y}$ ). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

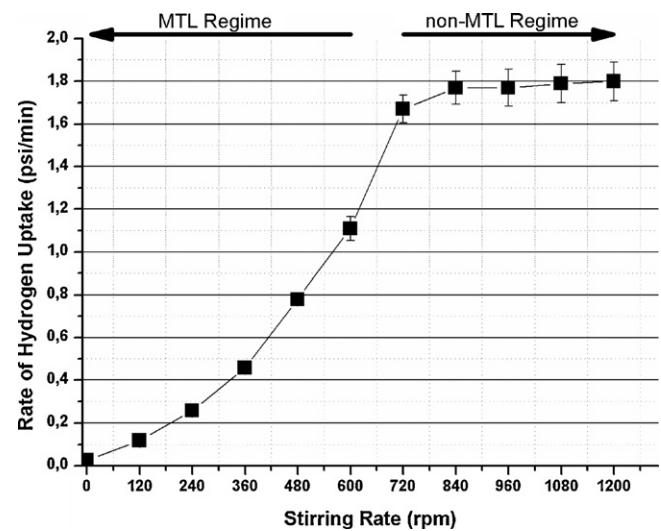
sodium cation distribution in the zeolite is essentially restored upon reduction. The cation sites left by  $\text{Ru}^{3+}$  ions upon reduction are reoccupied by sodium cations coming from sodium borohydride. Hence, host framework remains intact as shown also by XRD powder pattern (Fig. 3). However, the absorption bands of sodium translatory modes experience small red shift caused by the interaction with the ruthenium(0) nanoclusters in the cages of zeolite-Y. Hence, the small red shift observed in the site specific bands of sodium cation vibrational mode can be considered as evidence for the existence of ruthenium(0) nanoclusters within the cages of sodium reloaded zeolite-Y after reduction [29].

### 3.2. Zeolite framework stabilized ruthenium(0) nanoclusters as catalyst in hydrogenation of cyclohexene: evidence for a non-MTL (mass-transfer limitation) regime

In order to address the most important issue whether the hydrogenation reaction at the interface of gas and condensed phases



**Fig. 3.** The powder XRD patterns of zeolite-Y ( $\text{Na}_5\text{Y}$ ),  $\text{Ru}^{3+}$ -exchanged-zeolite-Y with a nominal compositions of  $\text{Ru}_{3.2}\text{Na}_{46.4}\text{Y}$ , and  $\text{Ru}(0)/\text{NaY}$  prepared by borohydride reduction of  $\text{Ru}_{3.2}\text{Na}_{46.4}\text{Y}$ .

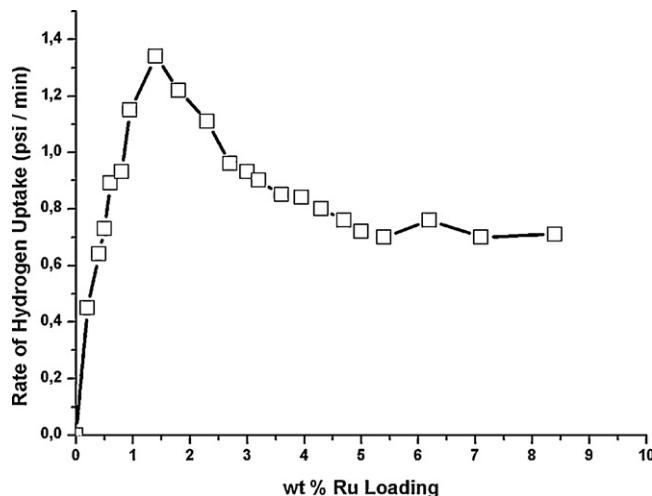


**Fig. 4.** Plot of hydrogenation rate versus the stirring speed during the hydrogenation of cyclohexene (0.5 mL in 1.5 mL cyclohexane) catalyzed by  $\text{Ru}(0)/\text{NaY}$  (100 mg with a ruthenium loading of 0.68 wt% corresponding to 0.0067 mmol Ru) in 1.5 mL cyclohexane at  $22 \pm 0.1^\circ\text{C}$  and  $40 \pm 1$  psi  $\text{H}_2$ .

is under mass-transfer limitation (MTL) regime [30], the dependence of reaction rate on the stirring speed was investigated. Eleven independent experiments were performed for the hydrogenation of cyclohexene catalyzed by  $\text{Ru}(0)/\text{NaY}$  under the same conditions ( $[\text{Ru}] = 3.36 \text{ mM}$ ,  $22 \pm 0.1^\circ\text{C}$  and  $40 \pm 1$  psi  $\text{H}_2$ ), but using different stirring speeds. The rate of cyclohexene hydrogenation was plotted against the stirring speed in Fig. 4. The inspection of the plot shows that the hydrogenation proceeds under non-MTL regime when the stirring speed is greater than 600 rpm. Additionally, in control experiments performed at a constant stirring speed of 720 rpm, doubling the catalyst concentration resulted in an increase in the hydrogenation rate by a factor of 2 (from 2.5 mmol benzene/h for 6 mM catalyst to 5 mmol benzene/h for 12 mM catalyst). This linear rate dependence on the catalyst concentration (*vide infra*) requires that the observed initial rate of hydrogenation is not influenced by mass-transfer limitation when the stirring speed is  $\geq 720$  rpm.

### 3.3. The effect of ruthenium loading on the catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene

Zeolite framework stabilized ruthenium(0) nanoclusters are also found to be very active catalyst in hydrogenation of neat benzene: a linear hydrogenation starts immediately without induction period as the catalyst is preformed (Fig. 4 elsewhere [19]).  $\text{Ru}(0)/\text{NaY}$  sample with a ruthenium loading of 1.4 wt% Ru provides a TOF value of 1040 mol benzene/mol Ru·h in the hydrogenation of neat benzene at  $22 \pm 0.1^\circ\text{C}$  and  $40 \pm 1$  psi  $\text{H}_2$ . The catalytic activity is expected to depend on the ruthenium loading of  $\text{Ru}(0)/\text{NaY}$  sample. In a series of experiments, the catalytic activity of  $\text{Ru}(0)/\text{NaY}$  samples (in all  $[\text{Ru}] = 10 \text{ mM}$ ) with different ruthenium loadings in the range of 0.4–8.4% was tested in the hydrogenation of neat benzene to determine the effect of ruthenium loading on the catalytic activity of  $\text{Ru}(0)/\text{NaY}$ . The variation in the catalytic activity of  $\text{Ru}(0)/\text{NaY}$  depending on the ruthenium loading given in Fig. 5 reflects the accessibility of ruthenium(0) nanoclusters in the zeolite cages by the substrate. The highest catalytic activity was obtained by using  $\text{Ru}(0)/\text{NaY}$  with a metal loading of 1.4 wt% Ru. Ruthenium(0) nanoclusters are most probably in the supercages ( $\alpha$ -cages), where the substrate can more readily access to ruthenium(0) nanoclusters compared to sodalite cages ( $\beta$ -cages) of zeolite-Y (Fig. 1(a)). As



**Fig. 5.** The rate of hydrogen uptake (psig H<sub>2</sub>/min) versus ruthenium loadings (wt%) for the hydrogenation of 1.0 mL benzene (11.2 mmol) catalyzed by Ru(0)/NaY (in all [Ru]= 10 mM) at and 40±1 psi H<sub>2</sub>.

the ruthenium loading increases, some of the nanoclusters might go to the less accessible sodalite cages as well or nanoclusters in the supercages become larger, blocking the entrance to the supercages.

#### 3.4. The catalytic activity of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene depending on ruthenium concentration and temperature

Ru(0)/NaY with a ruthenium content of ≈0.95 wt% were used as catalyst in the hydrogenation of neat benzene. Fig. 6 shows the plots of benzene concentration versus time during the hydrogenation of neat benzene (0.6 mL, 6.72 mmol) in the presence of Ru(0)/NaY in different ruthenium concentrations (2–12 μmol Ru) at 22±0.1°C. The rate of hydrogenation determined from the linear portion of the plots in Fig. 6 is in the range of 0.98–4.90 mmol benzene/h. Plotting the hydrogenation rate versus ruthenium concentration, both in logarithmic scales (the inset in Fig. 6), gives a straight line with a slope of 0.93≈1.0 indicating that the hydrogenation of neat

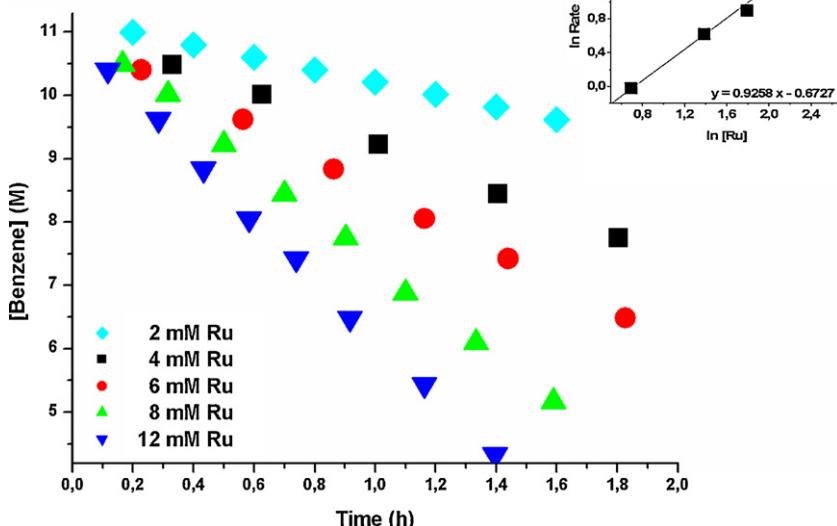
benzene is first order with respect to the ruthenium concentration. The hydrogenation of neat benzene (0.60 mL, 6.72 mmol) in the presence of Ru(0)/NaY (64 mg with a ruthenium loading of 1.1 wt% corresponds to 0.0069 mmol Ru) was carried out at various temperatures in the range of 15–35 °C at 40±1 psi H<sub>2</sub> and the results illustrated in Fig. 7 indicate the exceptional catalytic activity of Ru(0)/NaY even at low temperatures. The values of rate constant *k*, determined from the linear portion of the plot for each temperature (Fig. 7), are used to calculate the activation energy: Arrhenius activation energy was found to be  $E_a = 32 \pm 1$  kJ/mol for the Ru(0)/NaY catalyzed hydrogenation of neat benzene as shown in the inset of Fig. 7. The value of activation energy is lower than the value of 35 kJ/mol found for the hydrogenation of benzene catalyzed by platinum(0) nanoparticles [31], 36.5 kJ/mol for Ni-MCM-41 [32] and comparable with 30 kJ/mol for Pd/C catalyst [33].

#### 3.5. The catalytic lifetime of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene

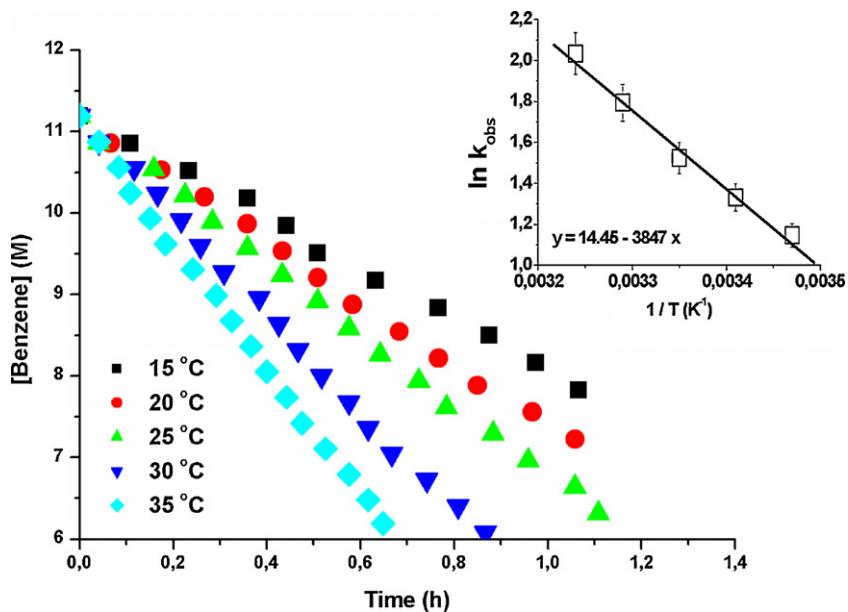
The catalytic lifetime experiment starting with 100 mg of Ru(0)/NaY (with a 1.4 wt% Ru loading) in 3.0 mL of benzene at 22±0.1 °C and 40±1 psi H<sub>2</sub> pressure reveals a total turnover number (TOF) of 2420 mol benzene/mol Ru and turnover frequency (TOF) value 1040 mol benzene/mol Ru·h before deactivation [19]. This is a record value since the highest TOF value known for neat benzene hydrogenation at room temperature is 960 mol benzene/mol Zr·h [12].

#### 3.6. The isolability and reusability of zeolite framework stabilized ruthenium(0) nanoclusters catalyst in the hydrogenation of neat benzene

The Ru(0)/NaY were also tested for their isolability, bottleability and reusability. After the complete hydrogenation of benzene catalyzed by Ru(0)/NaY, the catalyst was isolated as black powder by evaporating the volatiles in vacuum and further dried under N<sub>2</sub> purging at room temperature. Black samples of Ru(0)/NaY were bottled under nitrogen atmosphere and found to be stable for months. The isolated Ru(0)/NaY are redispersible in benzene, and yet still active catalyst in the hydrogenation of neat benzene. Fig. 8



**Fig. 6.** Plot of the concentration of benzene (mol/L) versus time (h) for the hydrogenation of benzene (0.6 mL, 6.72 mmol) catalyzed by Ru(0)/NaY with different ruthenium concentrations at 22±0.1 °C and 40±1 psig of H<sub>2</sub>. Inset: plot of the hydrogenation rate of benzene versus the catalyst concentration (both in logarithmic scale).



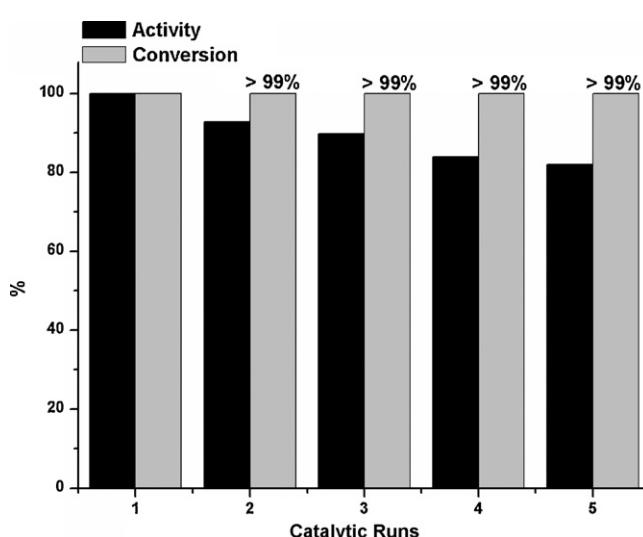
**Fig. 7.** Plot of the concentration of benzene (mol/L) versus time (h) for the hydrogenation of benzene (0.6 mL, 6.72 mmol) catalyzed by Ru(0)/NaY (64 mg with a ruthenium loading of 1.1 wt% corresponds to 0.0069 mmol Ru) at 15, 20, 25, 30, 35 °C and 40 ± 1 psig of H<sub>2</sub>. Inset: the Arrhenius plot for the hydrogenation.

shows the percentage of catalytic activity retained in the successive catalytic runs for Ru(0)/NaY catalyzed hydrogenation of neat benzene at 22.0 ± 0.1 °C. Ru(0)/NaY retain 81% of their initial activity and provides complete hydrogenation of neat benzene to cyclohexane even at the fifth run [34]. This result indicates that Ru(0)/NaY are isolable, bottleable, and yet catalytically active. The slight decrease in catalytic activity in subsequent runs may be due to the material loss during the isolation and redispersing procedure or due to passivation of nanoclusters surface. In a control experiment, no ruthenium was detected (by ICP, detection limit 24 ppb for Ru) in the filtrate obtained by filtration of the reaction mixture after the first run of hydrogenation. The hydrogenation experiment of fresh benzene performed by using the filtrate as catalyst, no hydrogen uptake was observed over 12 h. These experiments confirm the stability of ruthenium(0) nanoclusters, which retains within the

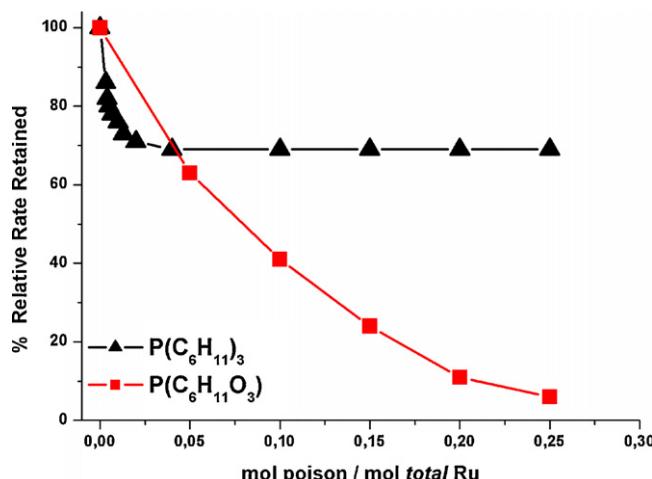
zeolite matrix (no ruthenium passes into the solution during the suction filtration). Another control experiment was also performed to show that the hydrogenation of benzene is completely stopped by the removal of Ru(0)/NaY.

### 3.7. $P(C_6H_{11})_3$ and $PC_6H_{11}O_3$ poisoning of zeolite framework stabilized ruthenium(0) nanoclusters in the hydrogenation of neat benzene

It is crucial in zeolite confined metal particle catalysis to know the percentage of catalytically active sites present on the external surface and/or inside the host material. To investigate the distribution of ruthenium(0) nanoclusters on the external surface or within the cages of zeolite-Y, a series of poisoning experiments for the Ru(0)/NaY catalyzed hydrogenation of neat benzene were performed by using two different phosphine ligands as poison; tricyclohexylphosphine ( $P(C_6H_{11})_3$ ), and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ( $P(OCH_2)_3CCH_2CH_3$  or shortly  $PC_6H_{11}O_3$ ), having kinetic diameters of 10.9 Å and 4.6 Å, respectively [35]. The hydrogenation of neat benzene catalyzed by Ru(0)/NaY was conducted in the presence of phosphine ligand in various phosphine/ruthenium molar ratio at 22.0 ± 0.1 °C. The initial rate of benzene hydrogenation was determined in each of independent experiments at various phosphine/ruthenium ratios and divided by the hydrogenation rate of neat benzene in the absence of phosphine at 22.0 ± 0.1 °C to obtain the relative activity (initial rate of benzene hydrogenation in the presence of poison over the one in the absence of poison). Fig. 9 shows the plots of relative hydrogenation rate of neat benzene versus the phosphine/ruthenium molar ratio for both of the phosphine poisons. In the hydrogenation experiments performed in the presence of  $PC_6H_{11}O_3$  the catalytic activity of Ru(0)/NaY decreases almost linearly with the increasing concentration of phosphine and the hydrogenation of neat benzene stops when 0.25 equivalents of  $PC_6H_{11}O_3$  per ruthenium is added to benzene (Fig. 9). The observation that the benzene hydrogenation is completely poisoned by less than 1 equivalent of phosphine is a compelling evidence for that it is a heterogeneous catalysis [36,37]. In poisoning experiments with  $P(C_6H_{11})_3$  the activity of the catalyst in the hydrogenation of neat benzene also decreases initially with the increasing phos-



**Fig. 8.** The percentage of catalytic activity retained and conversion of benzene (0.8 mL benzene corresponding to 8.96 mmol) to cyclohexane in the successive catalytic runs for Ru(0)/NaY catalyzed hydrogenation of neat benzene (100 mg with a ruthenium loading of 0.95 wt% corresponds to 0.0094 mmol Ru) at 22.0 ± 0.1 °C, 40 ± 1 psig of H<sub>2</sub>.



**Fig. 9.** Plot of percent relative catalytic activity of zeolite framework stabilized ruthenium (0) nanoclusters versus the poison/Ru molar ratio in the hydrogenation of neat benzene in the presence of  $\text{P}(\text{C}_6\text{H}_{11})_3$  or  $\text{PC}_6\text{H}_{11}\text{O}_3$  at  $22.0 \pm 0.1^\circ\text{C}$ ,  $40 \pm 1$  psig of  $\text{H}_2$ .

phine/ruthenium molar ratio up to 0.04, then remains unchanged beyond this ratio. The dissimilarity of two phosphine ligands in poisoning the Ru(0)/NaY catalyst in the hydrogenation of neat benzene arises from the size difference. While the small phosphine  $\text{PC}_6\text{H}_{11}\text{O}_3$  (kinetic diameter is  $4.6 \text{ \AA}$ ) can readily enter the supercages through the  $7.4 \text{ \AA}$  aperture of zeolite-Y [22], the large phosphine  $\text{P}(\text{C}_6\text{H}_{11})_3$  (kinetic diameter is  $10.9 \text{ \AA}$ ) cannot enter the zeolite cages, thus, remain outside. Therefore, the large  $\text{P}(\text{C}_6\text{H}_{11})_3$  can poison only the ruthenium(0) nanoclusters on the external surface of zeolite, while the small  $\text{PC}_6\text{H}_{11}\text{O}_3$  deactivates all the ruthenium(0) nanoclusters in the cavities and on the external surface of zeolite. The results of the poisoning experiments given in Fig. 9 indicate that the Ru(0)/NaY sample has 31% of catalytically active ruthenium(0) nanoclusters on the external surface of zeolite-Y and 69% in the cavities of zeolite-Y.

#### 4. Conclusions

The main findings of this work can be summarized as follows.

- (1) Ruthenium(0) nanoclusters stabilized by the framework of zeolite-Y, Ru(0)/NaY, can easily be prepared by ion-exchange of  $\text{Ru}^{3+}$  ions with the extra-framework  $\text{Na}^+$  ions in zeolite-Y and reduction of  $\text{Ru}^{3+}$  ions with sodium borohydride in aqueous solution all at room temperature.
- (2) The far-IR study of Ru(0)/NaY showed that the sodium cation site distribution in the zeolite is essentially restored upon reduction. The cation sites left by  $\text{Ru}^{3+}$  ions upon reduction are reoccupied by sodium cations coming from sodium borohydride. Hence, the host framework remains intact as shown also by powder XRD.
- (3) In addition to their record catalytic activity and lifetime [19], Ru(0)/NaY were also found to be isolable and reusable catalyst in the hydrogenation of neat benzene. Ru(0)/NaY isolated from the previous run retain 81% of their initial catalytic activity even at the fifth run in the hydrogenation of neat benzene at  $22.0 \pm 0.1^\circ\text{C}$ .
- (4) The tricyclohexylphosphine ( $\text{P}(\text{C}_6\text{H}_{11})_3$ ) and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ( $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ ) poisoning of Ru(0)/NaY in the hydrogenation of neat benzene showed that 31% of catalytically active ruthenium(0) nanoclusters are on the external surface whereas 69% of them locate inside the zeolite-Y.

- (5) Ru(0)/NaY catalyzed hydrogenation of benzene system is “relatively green” in its environmental impact in that it satisfies 7 of the 12 proposed principles of green chemistry [21] including that (i) it is 100% selective thus minimizing the byproducts or waste, (ii) it maximizes the incorporation of all reactants into the products, (iii) it is solventless (i.e., uses neat benzene as the substrate/solvent), (iv) it needs relatively low energy requirements due to its low temperature of  $22.0 \pm 0.1^\circ\text{C}$  and low pressure of  $\leq 3$  atm, (v) it is catalytic not stoichiometric, (vi) it does not use any blocking, protecting/deprotecting group, (vii) real-time monitoring is easy by following the  $\text{H}_2$  pressure loss or  $^1\text{H}$  NMR, for example.

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